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18. Auger electron spectroscopy, ethylene, dehydrogenation catalysts.

FINAL REPORT

SOLID LUBRICATION STUDIED BY OPTICAL MEANS

Grant No.: DAAL–86–G–0042

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ABSTRACT

The well–known and unwelcome phenomenon of the formation of carbon or coke on the surfaces of some clay and clay–supported transition metal cracking and dehydrogenation catalysts used in petroleum refining was applied to develop a process for the lubrication of tribo–surfaces at high temperatures by continuously regenerated surface carbon derived from flow of ethylene gas. Measurements with a pin–on–disc tribometer showed an immediate reduction of friction (from as high as 0.6 to as low as 0.05) and wear for nickel, palladium, ceramics coated with these metals and for bare silicon carbide and nitride at temperatures between 400 and 650° C and 0.2 MPa average Hertzian pressures, as soon as ethylene was introduced into the conjunction region. The environment could be air under ambient conditions. The carbon deposits were analyzed by Auger and Raman spectroscopy and ellipsometry and found to be generally about 400 Å thick and microcrystalline graphite or vitreous.

1. INTRODUCTION

The particular aspect of the tribology research in which the Fellow supported by this grant was to participate was, in the words of the Proposal "... to evaluate the effectiveness of solid lubricant films deposited on the surface of both metals and ceramics either by in situ formation or by chemical vapor deposition (CVD) or by sputtering or evaporation .... Silica and alumina... [and] metal oxides or metals, e.g. Pt on $A\ell_2O_3$, or Mo or Cr oxides, will ... become rapidly coated with carbonaceous or hydrated layers, which may be good lubricants. These observations originate from fluid and fixed bed petroleum cracking, with which the P.I. is familiar." The last sentence of the Program Description said: "The ultimate aim of the program is to show the direction for better (high temperature) solid lubrication."

The Tribology Research referred to was a major effort, also supported by the Army Research Office (Grant No. DAAL03–PG–0076). However, the small part worked on by the Fellow turned out to be the most successful.

After a relatively slow start in which various commercially available supported metal catalysts were examined and found unsuitable for tribological applications because of their physical form (common petroleum catalysts, such as $Ni/A\ell_2O_3$, are porous to have the largest possible surface area and are therefore mechanically weak), the work zeroed in on nickel alloys and palladium in contact with non–metallic (sapphire or quartz) counter–surfaces. Indeed the carbon formed by dissociative adsorption of a gaseous hydrocarbon, ethylene in particular, was found to be a good lubricant. Nickel was much more durable than palladium, because nickel forms a hard oxide on heating in air. Since silicon carbide and nitride have become ceramics of choice for applications in bearings and pistons run at high temperatures, say 500° C, they were coated with nickel and lubricated by the carbon formed catalytically from ethylene. The reason for this approach was the analogy with the nickel– and other transition metal–coated silica and alumina catalysts

that become covered with carbon or "coke" in petroleum cracking reactions. In other words, the original concept was followed. It turned out that lubricating carbon was still formed on rubbed silicon nitride and carbide surfaces even after the nickel coating was worn off. Therefore silicon nitride and carbide behave like the silica/alumina petroleum cracking catalysts, but only under mechanical stress, i.e. as part of a friction couple.

The economic potential of a high–temperature lubricating system using solid lubricants replenished by gaseous feeds is certainly significant. The underlying science which required sophisticated methods of analysis is new and likely to become widely applicable. It constituted the bulk of the research for which the fellowship was funded.

2. EXPERIMENTAL

2.1 Apparatus

The pin–on–disc friction tester shown in Fig. 1 was used for most of the work. The disc samples could be heated up to 650° C by radiation from a quartz halogen lamp. The inner shell, which had the shape of an ellipsoid of revolution, held the sample and the heater at its two foci and provided the test atmosphere, whose composition was controlled by gas flow meters. All experiments were run at atmospheric pressure. Since the inner shell was designed to be deliberately leaky, it was surrounded by an outer shell through which argon was flowing at a slow rate. It should be noted that the friction and wear tests were run at elevated temperatures, but the gases remained essentially at ambient temperature. The reasons for two shells, one within the other, were (i) control of gas composition without leak proof containers and (ii) avoidance of damage caused by minor explosions, since hydrocarbon/oxygen mixtures were sometimes tested. The effect of such an explosion was never more than a slight lifting of the inner shell's cover.

Most tests reported here were run with a 3/16" dia. pin, spherically tipped, of sapphire or metal and at 0.2 Mpa average Hertzian pressure and at sliding velocities

between 0.3 and 30 cm/sec (6 to 600 RPM), 4 RPM speed (i.e. 2 mm/sec. sliding velocity). With this test carbon could be generated on a surface and the friction brought about by this carbon could be determined simultaneously.

2.2 Test Results

2.2.1 Palladium and Nickel Surfaces

Ethylene–containing (10% ethylene in argon) atmospheres and palladium or nickel surfaces were studied. The metals were used either in the form of discs or pins running with ceramic counter faces, thus providing a metal transfer film on the ceramic's wear track. Both pure polycrystalline metals and alloys, possibly cemented with carbide materials (super alloys) were tested.

Fig. 2 shows the effect on friction of alternating exposures to oxygen and ethylene atmospheres for a "sapphire pin/aluminum oxide disc coated by a transfer film of palladium" combination. The sample temperature was 480° C. The rapid and essentially reproducible changes will be noted.

Since an objective of this study was to determine the role of diffusion on carbon formation and wear, the data of Fig. 3 were obtained. Clearly the process is sensitive to speed and load. Higher load causes a more rapid wear of the surface carbon and higher speed allows time for the carbon to reform between passes. Fig. 4 contains a similar map for 450° C, showing the pressure/time dependence more clearly for the three friction coefficients of 0.1, 0.2, and 0.3. The temperature dependence of the carbon coating's durability is brought out again in Fig. 5.

Another view of the temperature dependence is given in Figs. 6 and 7 where average coefficients of friction and pin wear were plotted against temperature for a series of 45 minute tests. Wear increases up to about 400° C after which the system begins to produce sufficient carbon to cause both friction and wear to drop dramatically.

The rate effect and temperature dependence are shown in Fig. 8, which shows the time (in seconds) required for the friction coefficient to drop to 0.1 after the introduction of ethylene. The same data were replotted the Arrhenius way in Fig. 9. From the slope an activation energy of 22 kcal/mole was deduced. This value is consistent with literature values for carbon formation on surfaces.

An effect of surface roughness is shown in Fig. 9 for data similar to those in Fig. 2. It would appear that surface roughness is much more important in the presence of oxygen.

The "carbon" produced by these experiments could be seen as well as demonstrated by optical and scanning electron microscopy. It effectively reduced friction and wear with increasing thickness generally up to about 50 nm on palladium. Greater layer thickness did not change friction and wear. The thicknesses were determined by ellipsometry, which also provided a measure of the orientation of the carbon layer. For the optical absorption index at 6328 Å came out to be about 0.1 ± 0.1, which checks the graphite value for basal plane orientation. For this orientation, as said earlier, graphite is a good lubricant even at high temperatures.

2.2 2 Nickel–Coated Alumina

Friction Measurements. Fig. 10 shows a typical friction record. The abscissa is distance (x) on the same circular track. Every tooth corresponds to one revolution of the disc whose bulk temperature was 500° C. The flash temperature in the contact was estimated to be over 600° C. In this particular case the friction coefficient μ decreased from 0.55 to 0.10 when the flow of ethylene of 400 mℓ/min was started. μ remained constant until the gas flow was turned off, which made μ go back to 0.55, but when the gas flow was resumed, it returned to 0.10. The $\pm$ dμ/dx's permit estimation of rates of carbon formation and wear.

Fig. 11 is a similar record, but this time the temperature was gradually increased

from ambient. At 400° C μ started to fall, reaching less than 0.05 at about 500° C presumably when the rate of carbon formation was optimized for the load, flow and speed conditions. Fig. 12 shows that reduction of the rate of ethylene flow from 800 to 400 mℓ/min increased μ while a return to the high flow rate brought it back down.

Surface Profiles. Both an optical (WYCO) and a stylus profilometer (FORM TALYSURF) were used. They both showed an initial surface roughness of about 0.25 μm RMS for the coated alumina disc. The depth of the wear track after repeated travel led to an average wear rate of 20 Å per minute when no ethylene was supplied. No wear was measureable when sufficient ethylene was supplied.

Composition Depth Profiles. Argon ion sputtering (ion milling) in conjunction with AES under ultrahigh vacuum conditions permitted depth profiling. Figs. 13a and b show composition profiles outside and inside the wear track. The former figure shows that nickel oxide extended to about 500 Å from the surface (point A), nickel to about 1000 Å where (B) aluminum oxide begins. No carbon was found outside the wear track. Fig. 13b shows carbon up to a depth of 1000 Å (C) where the carbon trace crosses the aluminum trace and the oxygen trace inflects. The nickel oxide (D) is now only 250 Å thick, having lost 250 Å as a result of wear during startup. These estimates are difficult to make more exact because of the initial surface roughness and will need refinement by calibration techniques. However, there is no doubt about the elemental composition.

Raman Spectra. The identification of the lubricating carbon is probably best done by Raman spectroscopy. Fig. 14 shows such a spectrum, which can be interpreted as either glassy carbon or graphite of crystalline size less than 25 Å. The former identification seems much more probable because graphite at random orientation would not be a

lubricant under our experimental conditions. If all the basal planes were located parallel to the surface, graphite crystals could conceivably lubricate. Although glassy carbon is reported to form at much higher temperatures than ours, the combination of flash temperature and pressure could lead to it. Glassy carbon is known to have a low friction coefficient.

2.2.3 Nickel–Coated Alumina, Coated and Bare Silicon Carbide and Silicon Nitride

Friction and Wear Measurements. Friction coefficients were recorded continuously with the calibrated strain gauge and some wear measurements were carried out by optical and stylus profiling of the disc surface across the wear track and by argon ion milling and Auger electron spectroscopy (AES), which measured wear–caused thickness changes of the nickel and nickel oxide overcoats. Fig. 15 shows records of coefficient of friction (μ) against sliding distance for silicon carbide. The mean surface temperature was 550° C, the average pressure on the sapphire pin 200 MPa, the ethylene gas velocity (when used) was 400 mℓ/min supplied to the conjunction region and the surrounding atmosphere was air. The linear speed at the contact was 3 cm/sec, but speeds as high as 30 cm/sec could be used. Fig. 15a is for the nickel–plated surface and Fig. 15b for the bare surface. The initial μ was 0.4 to 0.5 in either case but the drop to about 0.05 on introduction of ethylene occurred within 50 cm of travel for Fig. 15a but required about 1500 cm of travel for Fig. 15b. Clearly the nickel coating produces a faster reaction. When the gas stream was stopped the increase of μ was faster and the drop of μ on reintroduction of ethylene slower for the bare surface than for the coated one. Friction measurements on other samples were analogous. Propane could be substituted for ethylene, but then μ would drop only to 0.1. Wear of the lubricated surfaces was less than 20 Å/min.

Surface Compositions and Depth Profiles. Fig. 16 shows AES spectra of the

bare silicon carbide sample inside the wear track. The upper trace shows the composition before depth profiling (argon ion sputtering), the lower trace at a depth of about 300 nanometers. There is clearly less carbon and more silicon in the upper trace. This carbon must have derived from the ethylene since the silicon was essentially covered. Fig. 17 shows the corresponding depth profile. The outer carbon layer, probably surface contamination, is 50 Å thick. Next is a carbon layer of 200 Å thickness.

Fig. 18 shows high resolution AES spectra for the different substrates around the carbon peak at 272 ev. As pointed out by Rabalais and Kasi, the side bands are indicative of the type of carbon. These bands corresponding to the inside of the wear track are all very similar to those of standard graphite (top curve). There is no side band on the right side. On the other hand, the spectra corresponding to the carbon outside the wear track have somewhat less distinct features and, with only one exception, have a dip on the right–hand side, suggestive of carbidic carbon.

The Raman spectra of Fig. 19 were obtained to further differentiate between the carbon within the wear track and outside of it. These particular spectra refer to nickel–coated alumina but uncoated Sialon (silicon nitride containing alumina) gave very similar spectra. The 1370 cm^{-1} peak is better resolved inside the wear track than outside. There is also a frequency difference of the major band. These differences can be associated with smaller graphite crystal size (or vitreous carbon) inside the wear track.

3. DISCUSSION AND CONCLUSION

The most interesting result was the formation from ethylene of lubricating carbon not only on nickel, a known catalyst, but also on silicon carbide and silicon nitride (Sialon) when rubbed with an alumina (sapphire) pin. The reactions on the uncoated ceramic were somewhat slower, but still fast enough to make the use of this concept in machinery very promising. After all, what could be simpler than injecting a gas, such as ethylene, and

converting it to a solid lubricant (graphite–like) right on the wear surface. Since silicon carbide and nitride are hard to begin with, starting wear, i.e. until the operating temperatures are reached, was small.

The process developed does not require preheating of any lubricant, or a carrier gas, produces no solid deposit other than the lubricating carbon and does not attack the tribological surfaces chemically.

The ability to lubricate bare silicon carbide and nitride at high temperatures by the continuous formation of lubricating carbon from ethylene gas on the surface is very likely the most significant outcome of the Fellowship work and the related research project funded in part by the Army Research Office.

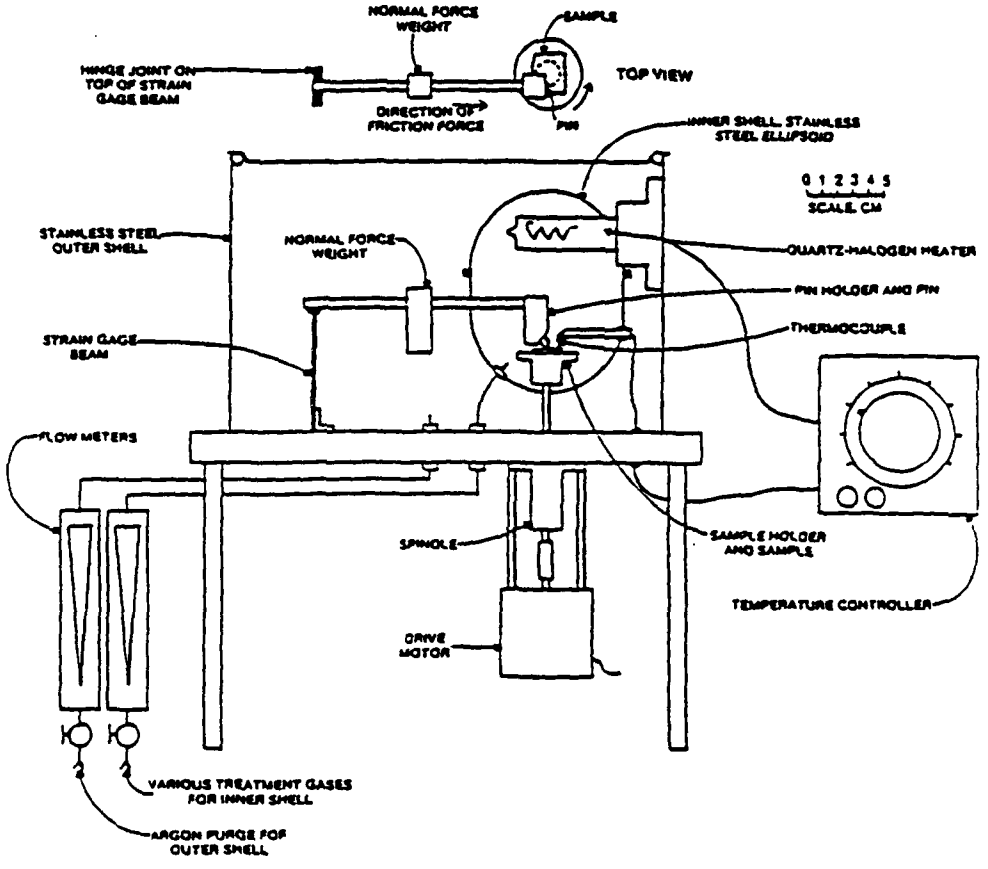

Fig. 1 High Temperature Controlled Environment Pin–on-Disc Friction Tester, Schematic Design.

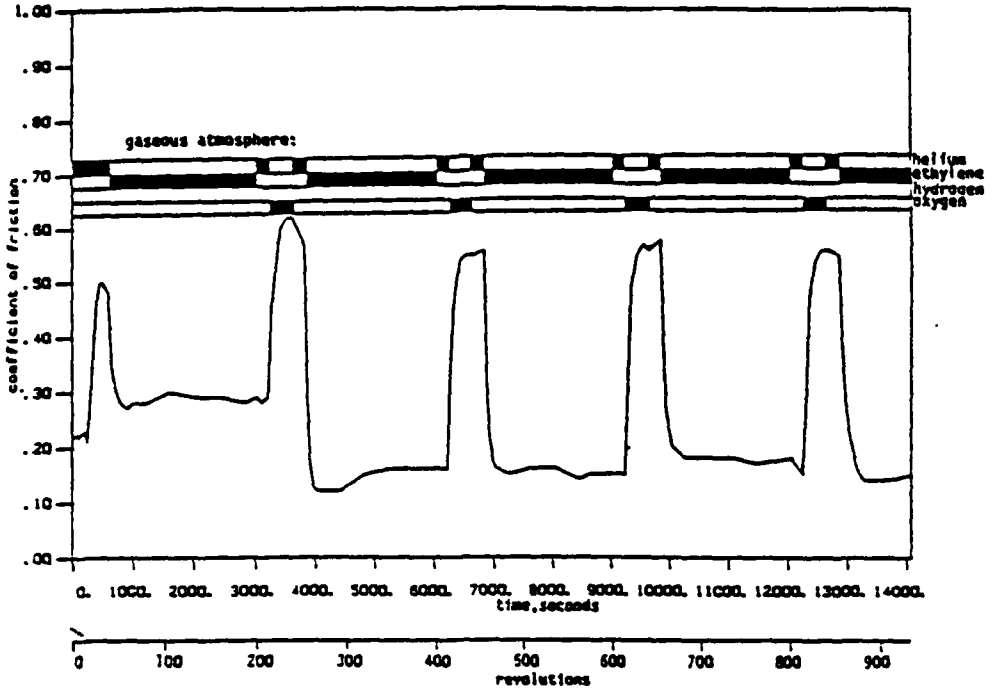

Fig. 2 Effect of Alternating Exposures to Oxygen and Ethylene Atmospheres. Sapphire Pin, Palladium Rubbed Film, and Aluminum Oxide Disc. 450° C, Run 69.

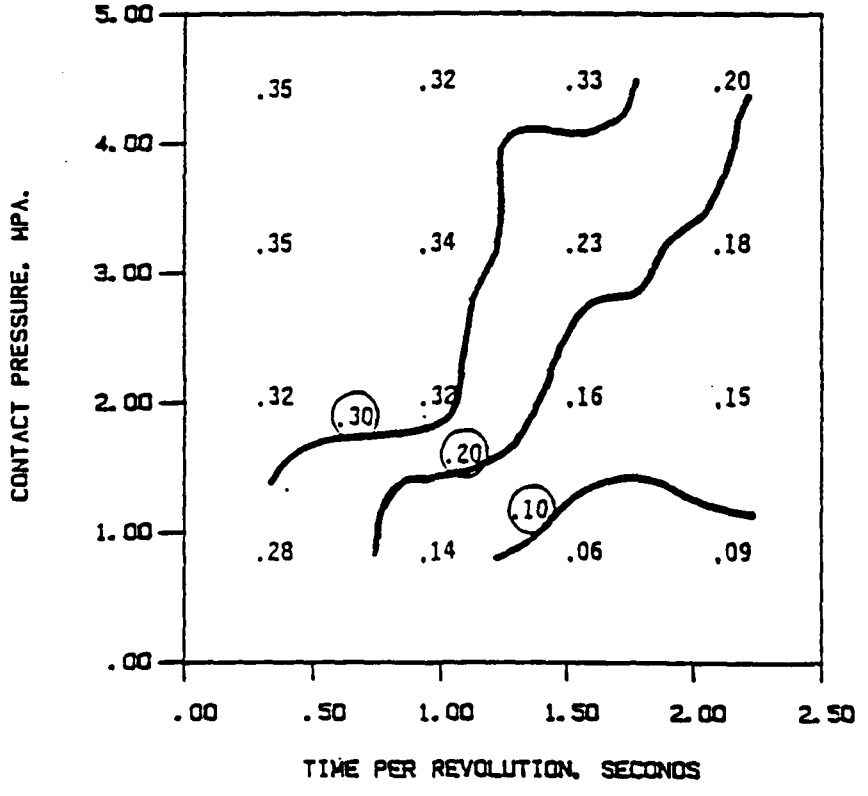

Fig. 3 Coefficient of Friction Map vs. Contact Pressure and Time per Revolution at 400° C. 1.0 mm Diameter Palladium Pin on Aluminum Oxide Disc. Run 87.

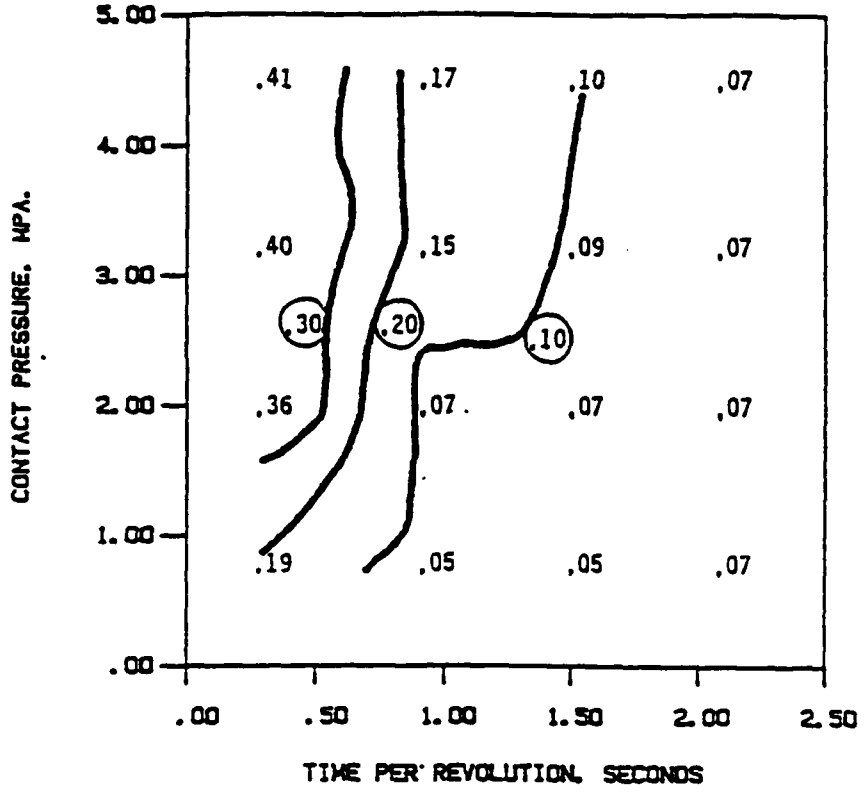

Fig. 4 Coefficient of Friction Map vs. Contact Pressure and Time Per Revolution at 450° C. 1.0 mm Diameter Palladium Pin on Aluminum Oxide Disc. Run 86.

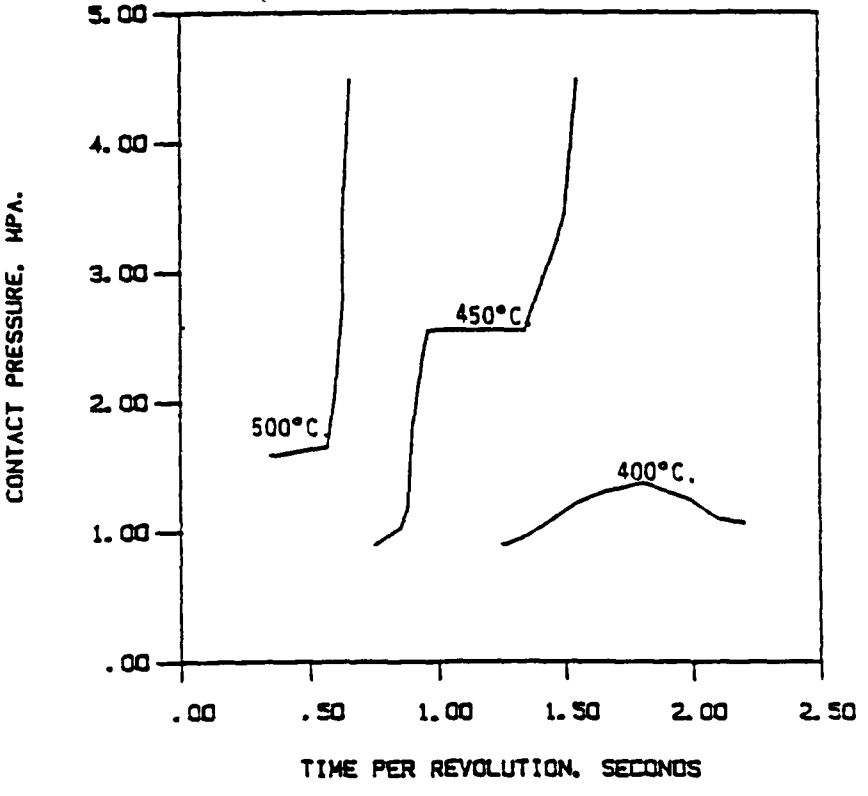

Fig. 5 Contour Plots of 0.10 Coefficient of Friction for Various Temperatures vs. Contact Pressure and Time per Revolution. 1.0 mm Diameter Palladium Pin on Aluminum Oxide Disc. Runs 86–88.

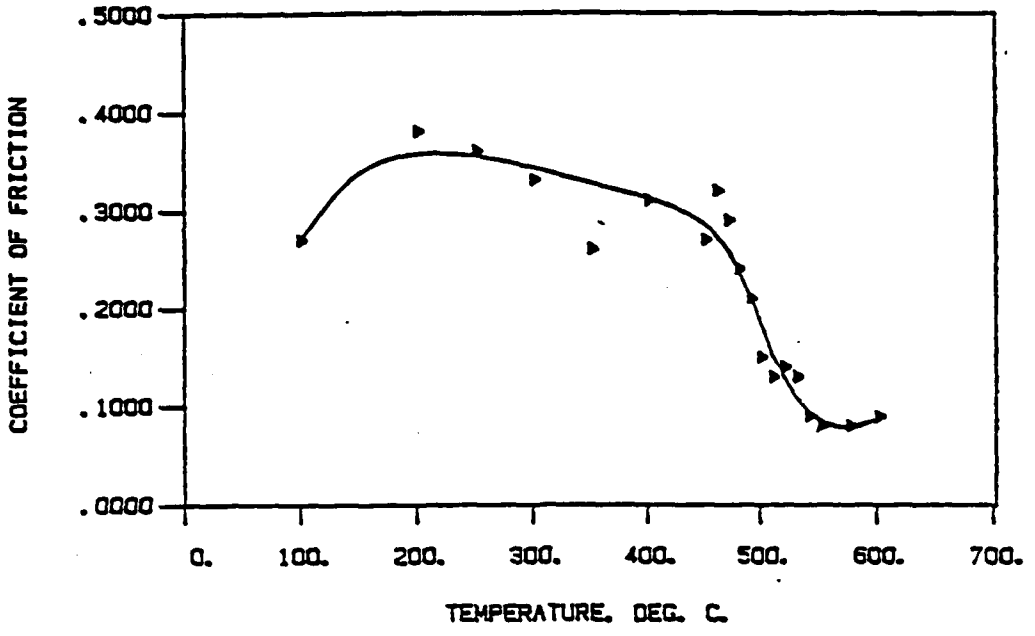

Fig. 6 Average Coefficients of Friction vs. Temperature for Wear Tests of 45 Minute Duration. Palladium Pin on Aluminum Oxide Disc. 373 Gram Load at 180 RPM, Runs 95–113.

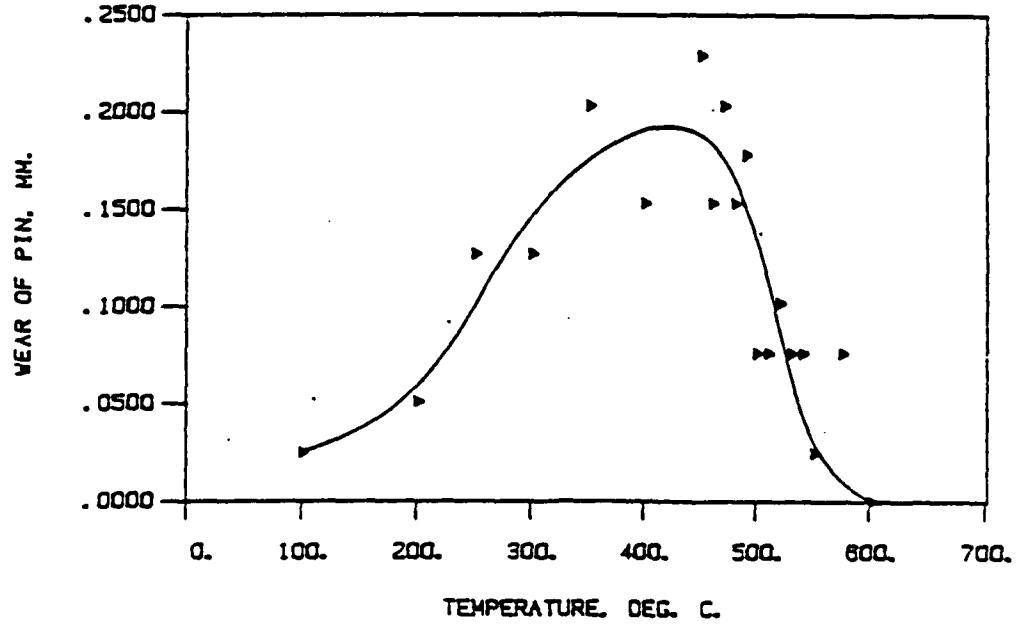

Fig. 7 Wear of Pin vs. Temperature for Wear Tests of 45 Minute Duration. Palladium Pin on Aluminum Oxide Disc. 373 Gram Load at 180 RPM, Runs 95–113.

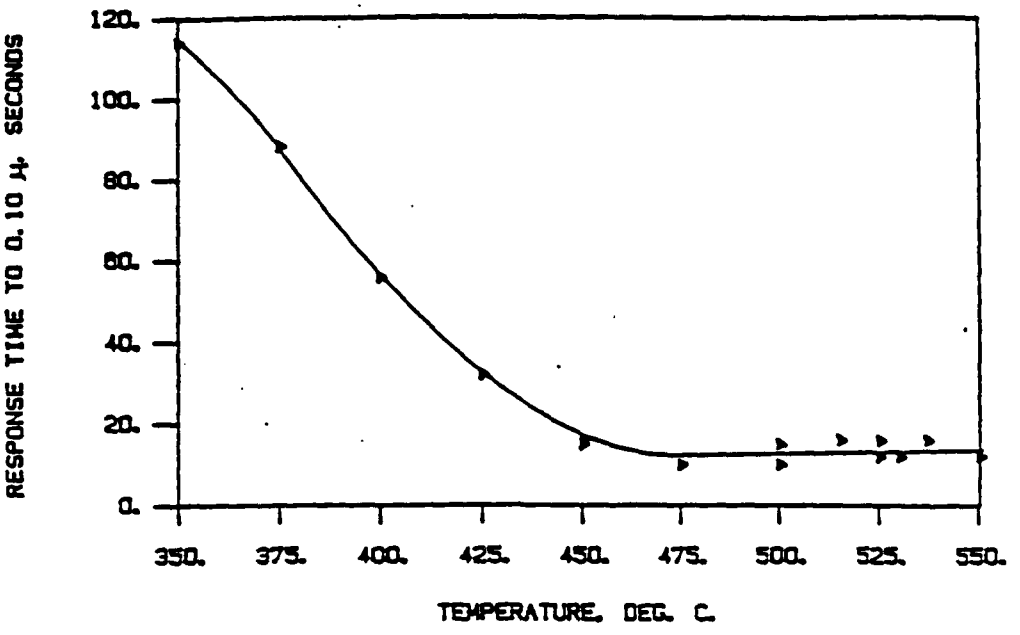

Fig. 8 Time of Friction Decrease for Carbon Formations as a Function of Temperature. Sapphire Pin on Nickel Disc. 202 Gram Load at 60 RPM. Runs 140–155.

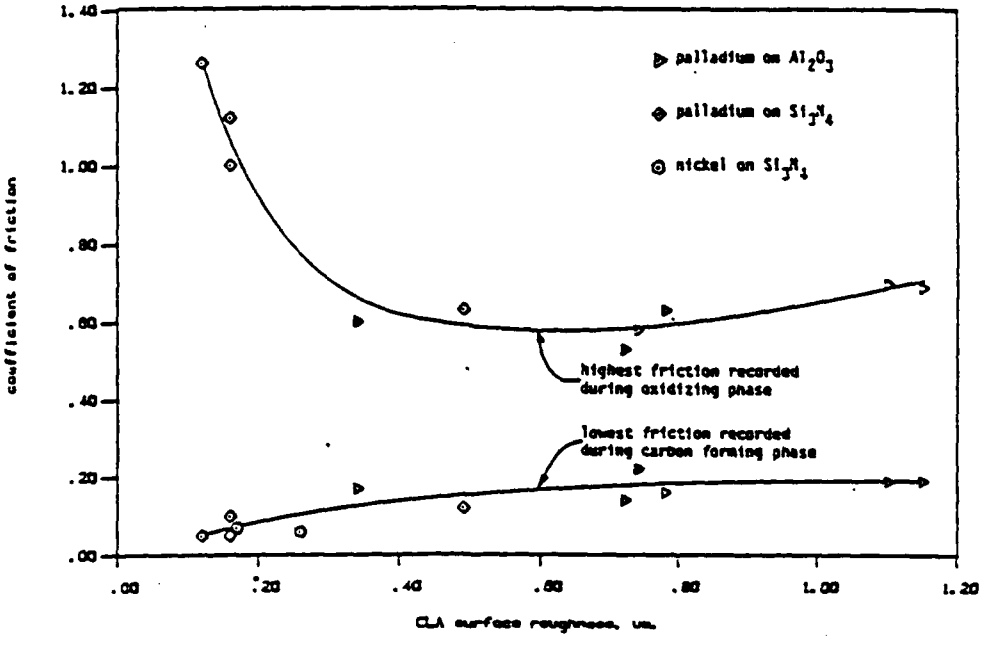

Fig. 9 Coefficient of Friction vs. CLA Surface Roughness Sapphire Pins, Metallic Rubbed Films and Discs as Noted. Runs 34, 35, 53–67, 71–74.

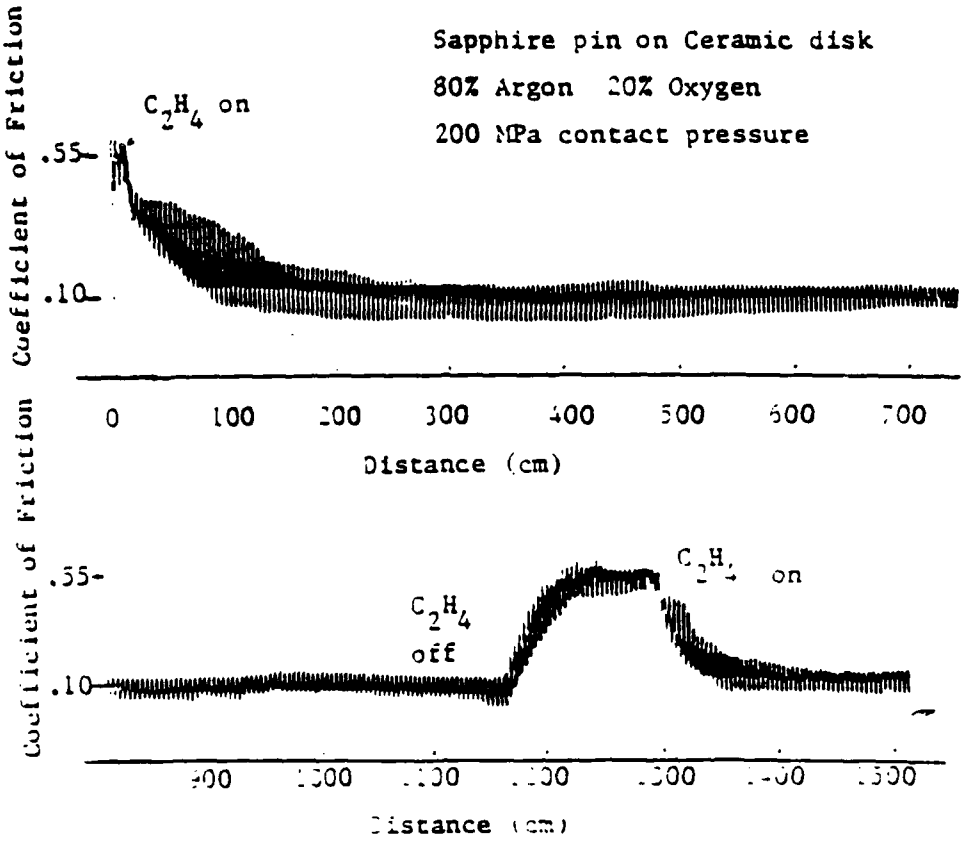

Fig. 10 Change of friction coefficient with travel distance and ethylene flow at 500° C. The linear speed was 3.5 cm/sec.

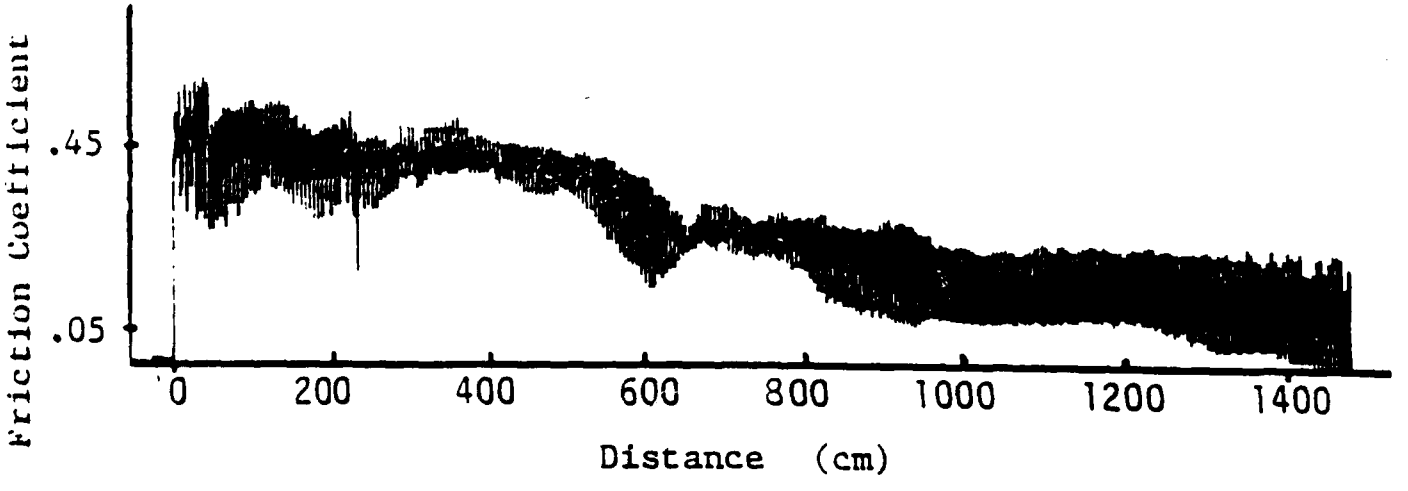

Fig. 11 Change of friction coefficient at 4.5 cm/sec speed with travel distance and rising temperature, starting from ambient.

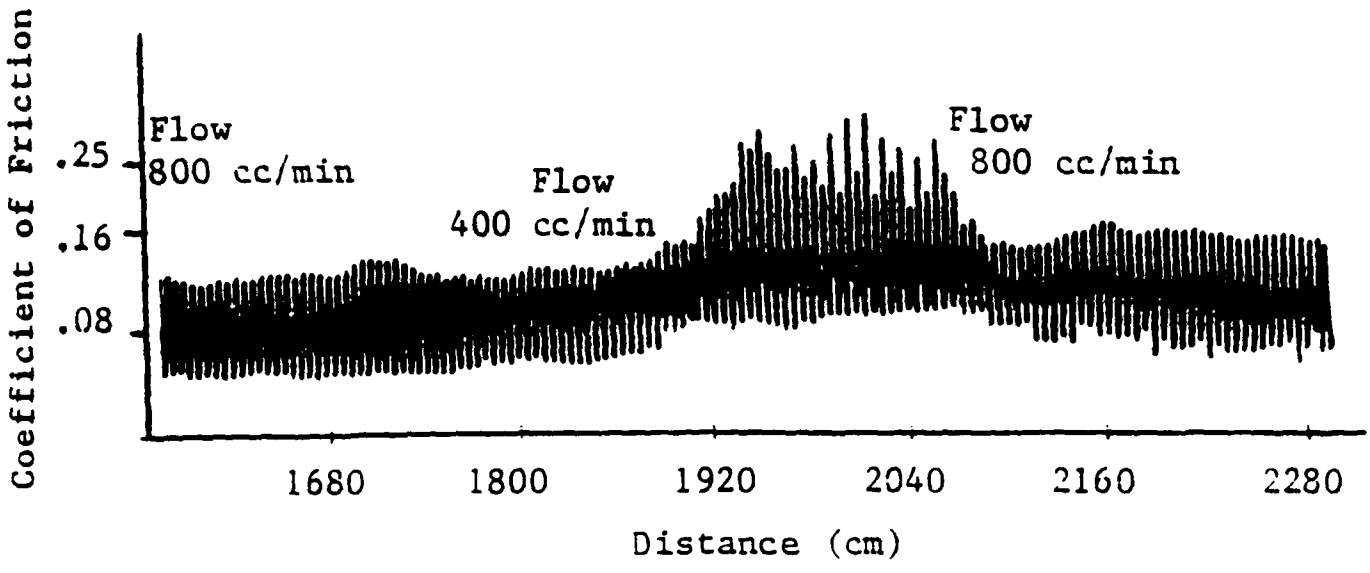

Fig. 12 Friction coefficient vs. ethylene flow rate at 9.5 cm/sec.

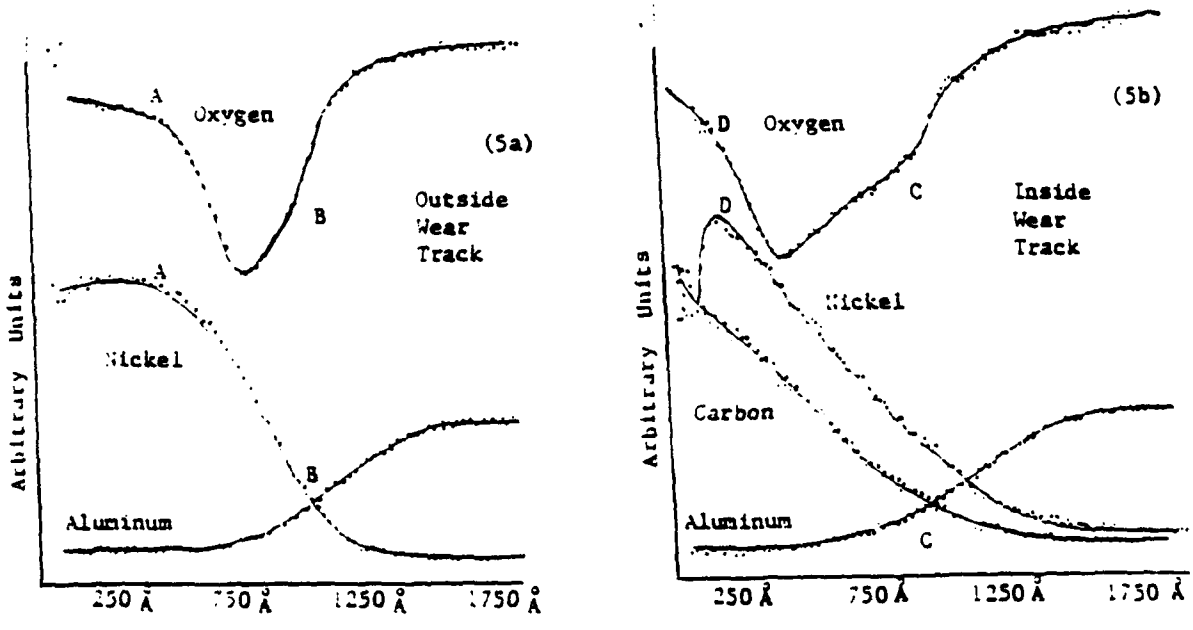

Fig. 13 AES depth profile of coated alumina disc; (a) outside, (b) inside the wear track.

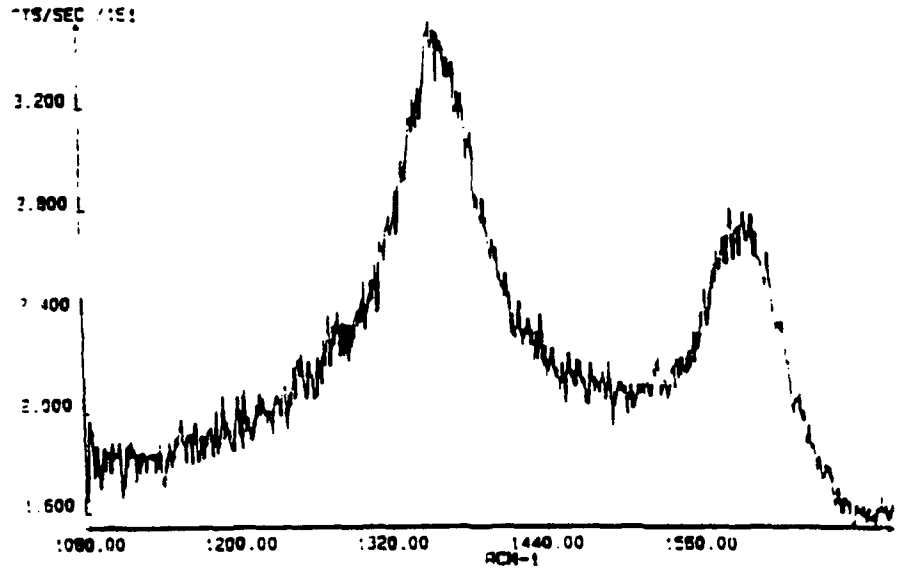

Fig. 14 Raman spectrum of carbon formed catalytically on nickel plate.

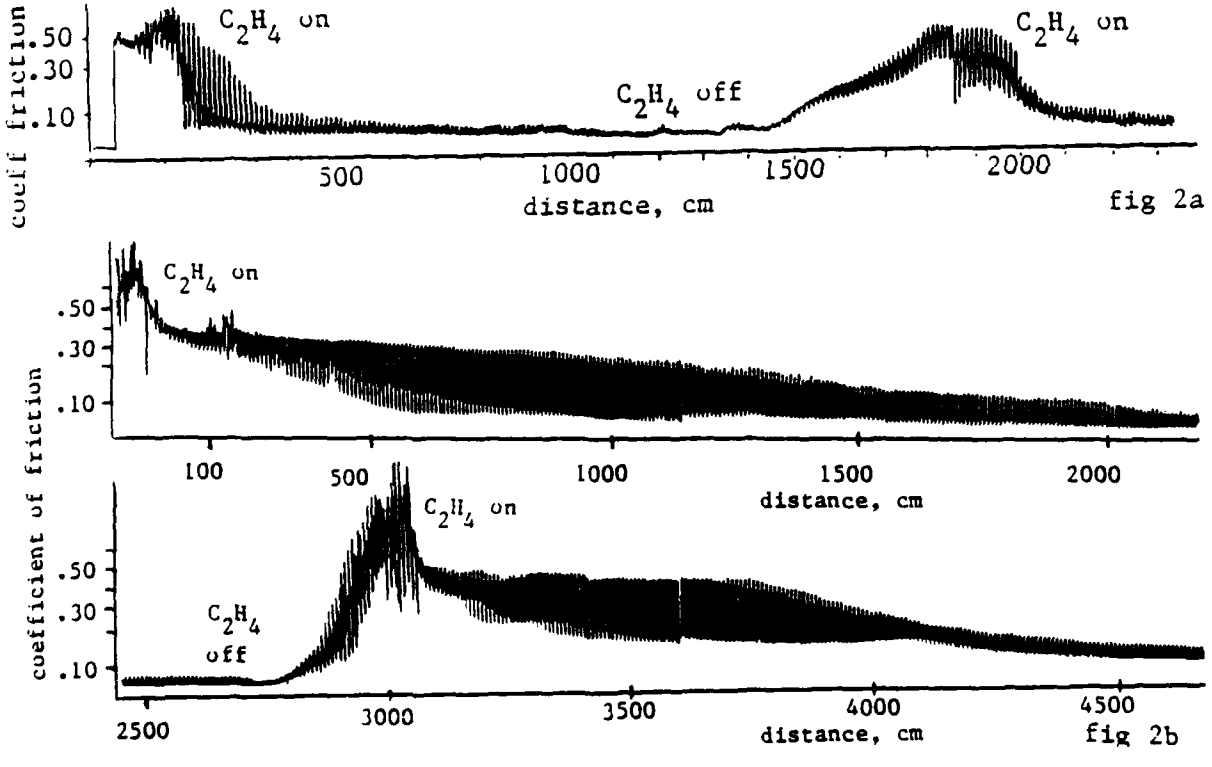

Fig. 15 Coefficient of friction vs. sliding distance for sapphire on nickel–coated silicon carbide (2a) and bare silicon carbide (2b). The ethylene reaction time is significantly longer without the nickel.

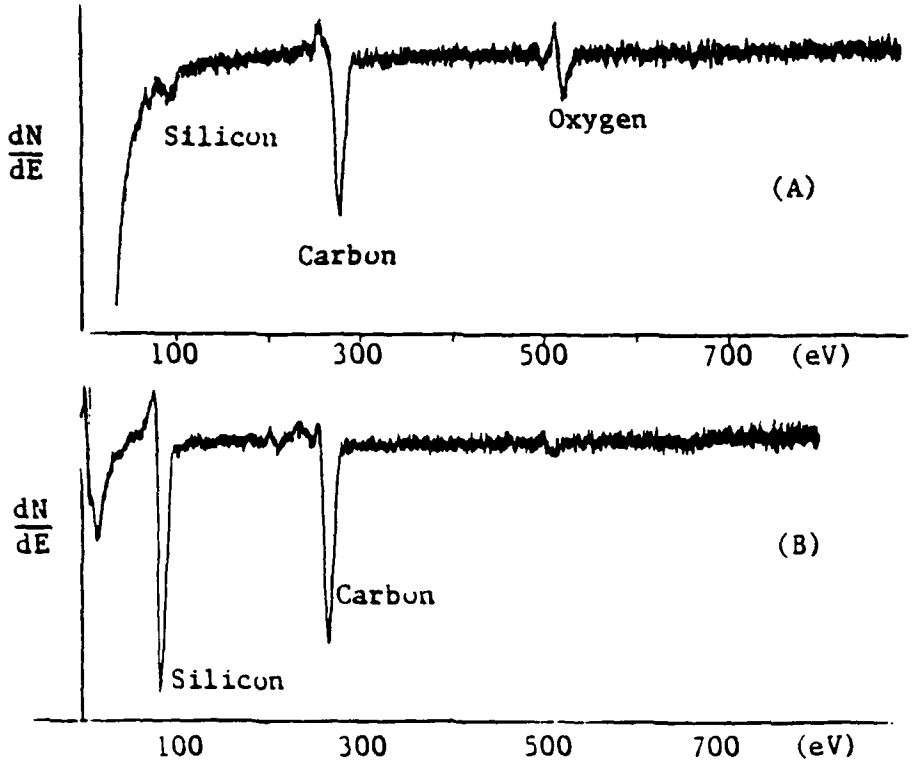

Fig. 16 Auger electron spectrogram of bare silicon carbide inside the wear track before and after ion milling. The silicon peak of the upper trace is obstructed by the carbon overlay.

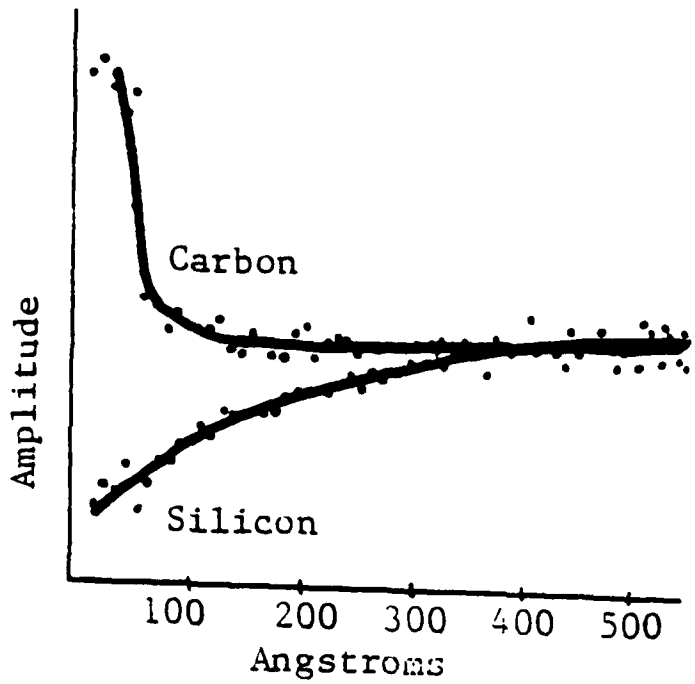

Fig. 17 Depth profile using Ar–ion milling through the carbon layer on the wear track of silicon carbide.

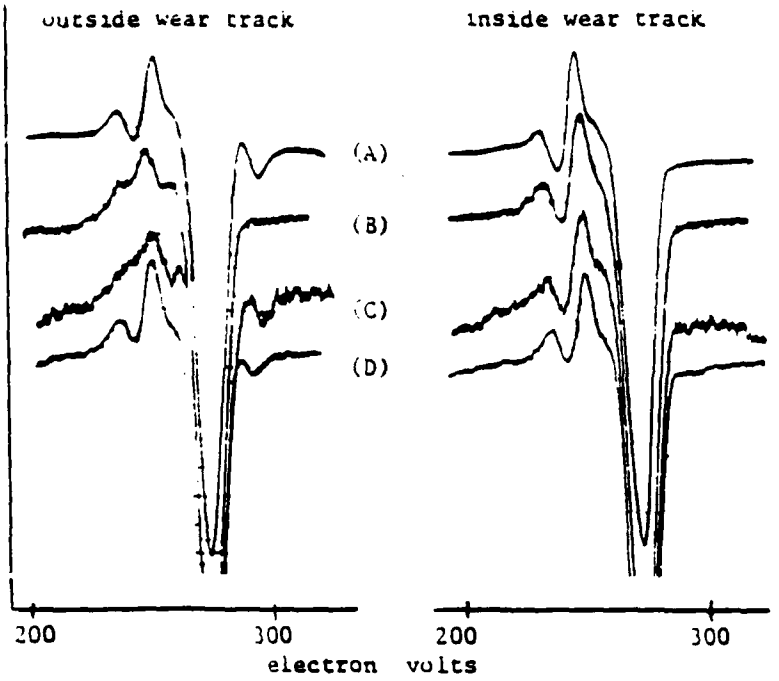

Fig. 18 High resolution AES of carbon present on the surface of nickel–coated Alumina (B), Sialon (C) and SiC (D). Trace (A), a reference, is sputtered carbon for outside and graphite for inside the wear track.

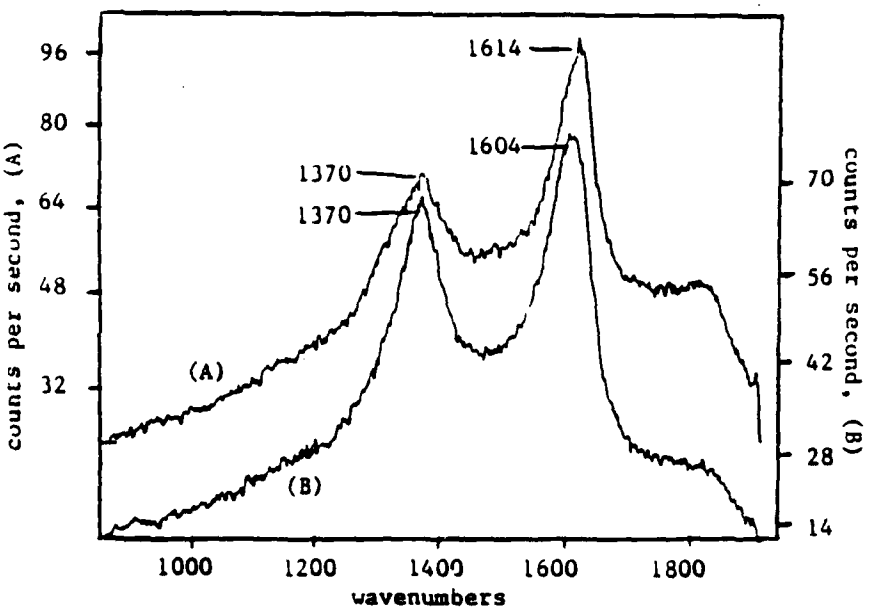

Fig. 19 Raman spectrograms of carbon deposited on nickel–coated alumina by ethylene; (A) outside and (B) inside the wear track.